Calculation of Transport Parameters of SiO₂ Polymorphs

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Silica polymorphs have been analyzed, that are similar to the amorphous phase of SiO₂; specifically, the α - and β -quartz, and the α - and β -cristobalite have been addressed. Two different *ab initio* methods have been used to calculate the full-band structure and the electronic properties of the polymorphs. In particular, the Hartree-Fock (HF) and Density-Functional Theory (DFT) approaches have been selected. A comparison of the energy-band branches and DOS shapes is reported, showing the similarities of the electrical properties that characterize the polymorphs under study. Finally, some relevant properties are compared for the analyzed set of polymorphs.

Keywords: Silicon dioxide; Full-band structure; Semiconductor devices; Silica polymorphs; Density of states; Transport properties

I. INTRODUCTION

Among insulators, silicon dioxide plays a major role in the solid-state technology. Especially in recent years, experimental and theoretical investigation have focused on microscopic properties of this material related with reliability problems. To accurately analyze the physics of damage and breakdown in VLSI devices, the microscopic properties of SiO₂ must be described, as well as those of the Si–SiO₂ interface. As far as the electron injection into the gate oxide is concerned, the description of the electron-energy distribution in an MOS device is fundamental

for a physically-based modeling. The carrier-distribution function in both Si and SiO₂ regions can be calculated by solving the Boltzmann Transport Equation (BTE). As the amorphous SiO₂ shows a number of electronic and optical properties in common with some silica polymorphs, it can be treated as a polar crystal. The SHE method, which solves the BTE basing on an expansion of the distribution function in spherical harmonics, proved to be a valuable tool for the analysis of semiconductor devices, in particular for hot-carrier effects [1]. The SHE method has been applied to silicon and silicon dioxide separately: in particular, for silicon a numerical

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full-band structure and the main scattering mechanisms have already been incorporated [2], while for silicon dioxide the collision-matrix contributions have been taken into account [3] in the frame of an analytical energy-band structure similar to that of [4]. The analysis of [3] shows that an accurate description of the dispersion relation and the density of states in energy in SiO_2 is necessary. For this reason the numerical calculation of such properties based on a full-band structure is addressed here.

Earlier calculations of the band structure for some polymorphs were based mostly on an empirical type of calculation (mixed-basis [5], pseudopotential [6]). In [7] a self-consistent LDA approach has been used, based on the assumption of a locally-homogeneous electron gas. In this work, *ab initio* calculations of the full-band structure have been worked out by means of two different techniques: Hartree-Fock (HF) and Density-Functional Theory (DFT), with the aim of overcoming some of the approximations adopted in [5–7]. Accurate calculations of both valence- and conduction-band structures, and of the corresponding densities of states (DOS), have been carried out. Moreover, the numerical results have been analyzed with particular emphasis on the parameters that influence the transport properties. First, the energy gaps have been compared: the HF method provides a smaller spread of values than the DFT for the polymorphs under study, but the values are overestimated with respect to the experimental ones. Then, the effective masses for the minimum of the conduction band have been extracted from the numerical data. Such calculation has been carried out only to the purpose of comparing our results with theoretical and experimental data shown in the literature, not to extract further information to be used in the calculation of the transport properties. Indeed, our aim is that of incorporating the numerical full-band structure within the transport solver SHE without any simplification, similarly to what we have already done for silicon [2].

II. THEORY AND COMPUTATIONAL DETAILS

The calculation of the band structure and DOS can be dealt with by methods similar to those used for analyzing molecular structures. Among these are the HF and DFT methods which are implemented in the code CRYSTAL98[®], adopted in this work. In the HF method the N -electron problem is reduced to a system of coupled single-electron equations that minimizes the total energy of the system. In the DFT level, the system is approximated by N non-interacting electron equations that give the same electron density. In the exchange- and correlation-potential terms, the Becke and Lee-Yang-Parr extensions for the local density approximation have been adopted. The crystalline space groups for the set of silica polymorphs are taken from [8]. The lattice parameters were calculated as in [9], starting from the experimental values by Wickoff [8] and minimizing the HF unit cell energy. In Table I the crystalline symmetries and the lattice parameters of the SiO_2 polymorphs are reported.

Finally, the basis sets, that are the sets of normalized Gaussian functions used by the solver to calculate the atomic orbitals, have been chosen among the optimized sets listed in [9]: the choice of the basis set plays an essential role in the description of the electronic structure, in particular for an accurate determination of the conduction-band eigenvalues. In Table II, the adopted basis

TABLE I Crystalline symmetries and lattice parameters of the SiO_2 polymorphs

Polymorph	Crystalline symmetry	Lattice params. (Å)
α -quartz	Trigonal	$a = 4.9138$
	$P3_221$	$c = 5.4052$
β -quartz	Trigonal	$a = 4.996$
	$P6_222$	$c = 5.497$
α -cristobalite	Tetragonal	$a = 4.971$
	$P4_12_12$	$c = 7.010$
β -cristobalite	Cubic	
	$Fd3m$	$a = 7.313$

TABLE II Adopted basis sets for silicon and oxygen

Atoms	Basis set	Gaussian exponents
Si	6-21G(2d)	$\alpha_{sp} = 0.13$
		$\alpha_{d1} = 0.5$
		$\alpha_{d2} = 1.5$
O	6-211G(2d)	$\alpha_{sp1} = 0.89$
		$\alpha_{sp2} = 0.28$
		$\alpha_{d1} = 0.4$
		$\alpha_{d2} = 1.2$

sets are reported for the silicon and oxygen atoms, respectively. More details of the adopted approach are given in [10].

III. RESULTS

As output of the HF and DFT calculations, the ground-state energy per unit cell, the pattern of the highest-valence and lower-conduction bands, and the densities of states have been analyzed. In Table III the minimum energy values by HF calculations are reported, compared to the DFT ones: it is worth noting that the basis-set coefficients have been optimized in order to minimize the ground-state energy in the HF level. The bands have been calculated along the high-symmetry lines of the first Brillouin zone specific to each polymorph [11]. The energy interval investigated in this work ranges from 2–3 eV below the maximum of the highest-valence band to about 6 eV above the minimum of the lowest-conduction band: the number of branches is rather large. In order to give sensible examples of the obtained results, the calculated band structures of α -quartz and β -cristobalite are shown in

TABLE III HF and DFT ground-state energy per unit cell (GSE) calculated by the solver

Polymorph	GSE HF (a.u.)	GSE DFT (a.u.)
α -quartz	-1316.1433	-1319.8277
β -quartz	-1316.6522	-1320.3080
α -cristobalite	-1754.8537	-1759.7498
β -cristobalite	-877.4220	-879.8614

Figures 1 and 2, respectively. The branches have suitably been grouped in order to present the result in a compact form; the origin of the energy scale coincides with the maximum of the valence band or the minimum of the conduction band as the HF and DFT values of the energy gap are different. The number and shape of the bands differ from one polymorph to another due to the different characteristics of their unit cells. The density of states in energy per cell (DOS) is reported in Figure 3 for α - and β -quartz, and in Figure 4 for α - and β -cristobalite. It is worth noting that each polymorph is characterized by a different number of branches for a given energy interval: as the total density of states is the sum

FIGURE 1 α -quartz: full-band structure calculated with HF method (continuous lines) and with the DFT method (dashed lines).

FIGURE 2 β -cristobalite: full-band structure calculated with HF method (continuous lines) and with the DFT method (dashed lines).

of the densities related to each branch, α -cristobalite (with a 12-atom unit cell) exhibits higher DOS values than β -cristobalite (6-atom unit cell). The energy band and DOS calculated with the two methods are usually similar in shape. The DFT eigenvalues are in general slightly lower than the HF ones. Moreover, the energy-band gap is usually overestimated by the HF method and underestimated by the DFT one with respect to the experiments. On the other hand, the calculated energy-band gaps for the investigated polymorphs differ from each other by less than 1 eV. In Figure 5, the normalized energy-gap values $E_{\text{GAP}}(\text{polymorph})/E_{\text{GAP}}(\alpha\text{-quartz})$ are reported for the set of polymorphs

FIGURE 3 Density of states in energy for α - and β -quartz. Solid lines: HF; dashed lines: DFT.

FIGURE 4 Density of states in energy for α - and β -cristobalite. Solid lines: HF; dashed lines: DFT.

under study for both HF and DFT levels: a difference less than 15% is obtained in both sets of data, this showing that the silica polymorphs have a number of electronic properties in common, due to the similar microscopic density. In order to quantitatively compare the results given by the two methods for the set of polymorphs, the effective masses of the lowest-conduction band have been calculated along the three main directions. In Figure 6 the effective

FIGURE 5 Normalized energy-gap values of the silica polymorphs.

FIGURE 6 Effective masses of the silica polymorphs.

masses, obtained as a geometrical average between the three values along the main directions, are reported for the set of polymorphs under investigation. The values of the masses calculated by the DFT method are rather similar, this confirming that the silica polymorphs are similar. The results given by the DFT approach are in good agreement with the values reported in [4–7]. In contrast a discrepancy is found in the HF data, in particular for the α -cristobalite: this is probably due to the adopted basis set, that has been optimized for α -quartz.

IV. CONCLUSIONS

A selected set of silica polymorphs have been analyzed, with the aim of taking into account forms that are similar to the amorphous phase of SiO_2 . The investigation has been carried out in the frame of the HF and DFT approximations, using CRYSTAL98[®]. The energy-band branches and DOS shapes have been calculated, and the effective masses have been computed as well. Even if the HF and DFT methods used in the analysis usually provide energy-gap values that differ from the experimental ones, the band structure and DOS are in good agreement with results by other methods, and can be indicated as a good description of the electronic properties for the material under study.

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